Influence of impurities such as C, Al and Cu on the melting behavior of LIB cathode materials under inert and reducing atmospheres

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a. **KEYWORDS:** Lithium-Ion Battery, Circular Economy, Pyrometallurgial Recycling, InduRed, InduMelt

INTRODUCTION

The electrification of energy intensive industries is often highlighted as one of the major milestones to reach international climate targets. However, by an increased demand of renewable energies the importance to provide buffer solutions increases [1]. Lithium-Ion Batteries (LIB) have shown to be the most prominent alternative to fulfill not only mandatory characteristics such as energy- and power density, but also safety properties and durability. Although a LIB often surpasses a lifespan of 10-15 years, at the end-of-life (EoL) of a LIB, the state of health (SOH) is often too low to be used in a second life application [2]. To increase economic independence, it is of utmost importance to keep valuable metals within Europe and therefore develop efficient recycling methods. However, state-of-the-art recycling technologies are not capable to recover targeted recycling rates and are all facing more or less severe bottlenecks. Although hydrometallurgical recycling approaches already achieve recycling efficiencies of up to 100 wt.-%, they are very sensitive to a fluctuating input material. Since it is hardly possible to determine the cathode chemistry used in a battery, there is bound to be a highly fluctuating waste stream. Pyrometallurgical recycling methods are more or less insensitive to varying input material, however they face the problem of lithium (Li) slagging. Furthermore, the high energy demand is often based on conventional energy sources such as oil and gas and are therefore ecologically unfavorable [3]. To counteract these bottlenecks, at the Chair of Thermal Processing Technologies at Montanuniversitaet Leoben, a novel pyrometallurgical recycling concept, the so-called InduRed reactor was developed.

MATERIALS AND METHODS

The InduRed reactor concept and its batch version, the so-called InduMelt reactor, described in Wiszniewski et.al 2023 [4], is a novel pyrometallurgical recycling facility for spend LIB. Originally developed to extract gaseous phosphorous (P) via the gas stream from sewage sludge ashes, the InduMelt plant offers ideal conditions to recycle active material, also called black matter – a mixture of cathode- & anode material and additional components such as copper (Cu) or aluminum (Al) – from spent LIB. The main components of the InduMelt plant are a cylindrical MgO crucible with a domed bottom, filled with layers of 10 – 15 graphite cubes. An induction coil is placed around the crucible to provide the necessary magnetic field to heat-up the graphite cubes, solely integrated to function as susceptor material and provide a huge reaction surface. As result of the high contact area a thin melt film occurs, offering short diffusion paths and -ways and therefore allows volatile components such as Li or P to be removed via the gas phase. With carbon (C) as part of the anode material, a reducing atmosphere with a high CO/CO_2 ratio is ideal for the reduction of the lithium-metal-oxides (LMO) [5].

To further investigate the high-temperature behavior of LIB cathode materials, several experiments within a heating microscope (Hesse Instruments EM 201 with an HR18-1750/30 furnace) were carried out by Baldauf [6] and Holzer et. al. [7]. The result of this test series, was to provide a contour diagram which visualizes the changes of the cross-sectional area of the samples over temperature, in order to determine necessary melting ability required for the InduMelt plant. To simulate expected waste stream compositions, additional impurities, such as C – originating from the anode material – and Al – resulting from the electrode conductor foil – were added and mixed together. A sample with a mass of approximately 0.1 g was pressed in a standardized cylindrical form and placed on an Al_2O_3 analysis plate. To prevent oxidation reactions, the combustion chamber was purged with 2 l/min of argon (Ar) gas, thus resulting in an oxygen poor atmosphere. The sample was then heated up to a temperature of around 1600°C with a maximum heating rate of 80 K/min.

To guarantee a successful reduction process without further laboratory analyses, all samples were tested for magnetic properties. As result of the inert atmosphere, the stoichiometric carbon demand for complete reduction of the input materials and a conversion of the supplied C to CO_2 instead of CO, was between 10 and 11 wt. %, rounded. With this ratio as baseline, C and Al were added in different concentrations to determine limitations of input impurities for the InduMelt reactor design [6]. Based on a series of tests within the heating microscope, an interpolation network of 1500 points was generated in order to generate a heat stratification diagram [7]. In order to simulate the influence of possible impurities on the melting behaviour and thus a waste stream that is as real as possible, further tests were carried out with additional Cu in the heating microscope [8]. To further analyze the influence of a reducing atmosphere occurring in the InduMelt plant, another heating microscope (Hesse, EM301) was used for melting trials, purged with CO gas.

RESULTS

As described in Materials and Methods, heating microscope trials with varying chemistries were the basis for the examination of the contour diagrams and thus a possible processing window for the InduMelt plant. In figure 1a the influence of C, C and Al and the combination of C, Al and Cu can be seen under inert atmosphere with Ar purge gas. First major outcome of this series was, that with addition of carbon (NCA_C8.0) the melting behavior could be improved with a parallel reduction process, resulting into a magnetic metal phase. Furthermore, since Al acts as even stronger reducing agent than C, an oversupply above the stoichiometric demand of about 11 wt.% of reducing agents, led to a poorer melting ability (NCA_C8,0_Al4,0). Additionally, an Al amount of more than 6 wt.% led to strong aluminothermic reactions, resulting into test failures. The addition of copper resulted mostly into a bloating behavior at lower temperatures, as result of the degasification of humid components and a positive effect on the melting behavior, reducing the temperature of the first melting point on average between 35°C to 135°C. As Cu might also works as reducing agent, an oversupply, resulting into poorer melting behavior, should be avoided.

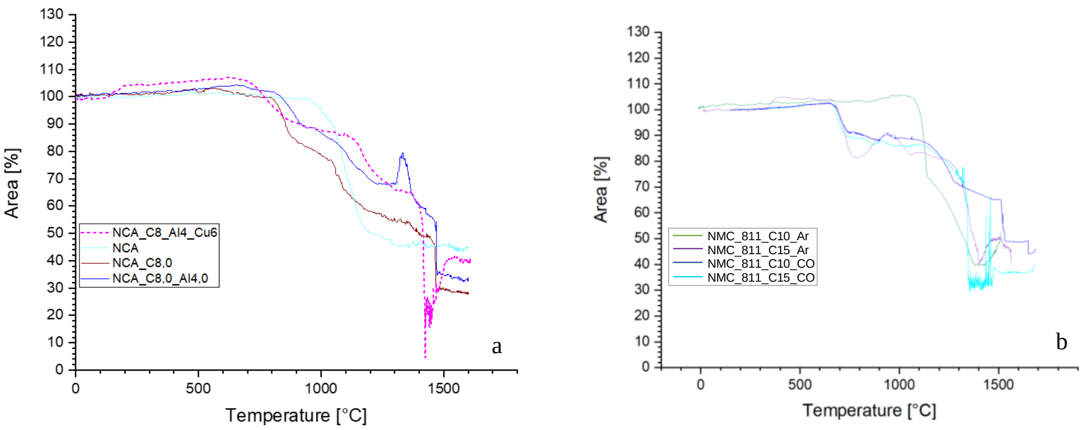

Fig. 1. Heating microscope trials with LIB cathode material NCA. Fig. 1a: Influence of C, Al and Cu on the melting behavior of NCA under inert atmosphere [6, 8]. Fig. 1b: Influence of C on the melting behavior of NMC_811 under inert and reducing atmosphere.

By implementing the before mentioned interpolation network, a contour diagram with approximately 1.500 data points was generated. In addition, an upper and lower limit of the data points was implemented, whereby the lower limit (32.87 %) marks the range at which there is sufficient meltability for the InduMelt and the upper limit (49.13 %) at which insufficient meltability has occurred. The area between the boundaries marks a transition area where partial melting of the samples has occurred. Compared to the results of Baldauf [6] without Cu, the influence of Cu led to an increase of the transition range by 7.36 %, resulting in a reduction of the range of non-meltable mixtures [8]. Figure 2 provides an overview about the influence of different carbon and aluminum concentrations with fixed copper content at 1550°C.

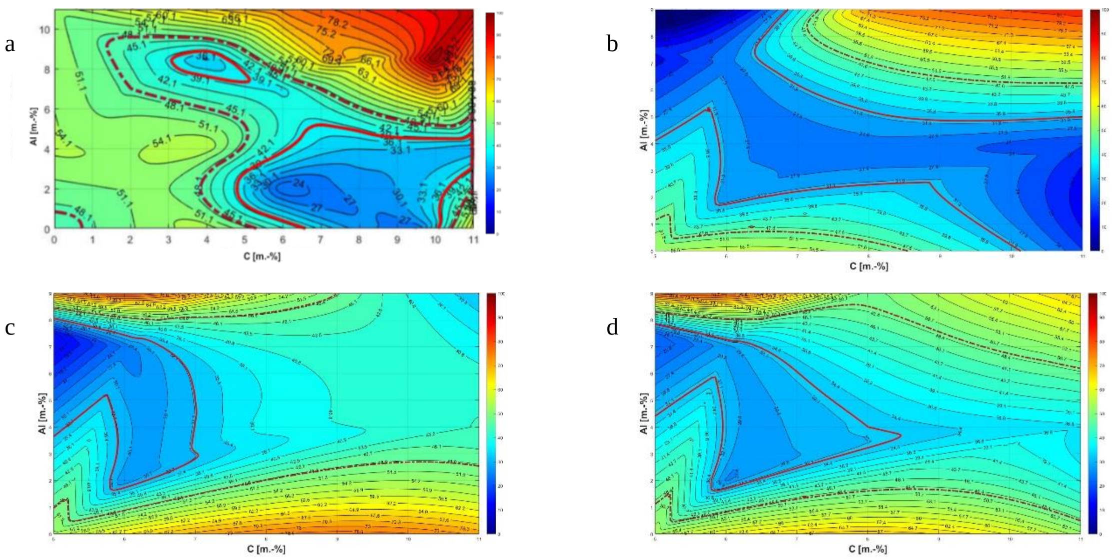

Fig. 2. Interpolation network: Change in cross-sectional area of the cathode material NCA with varying C and Al contents with fixed Cu contents at 1500°C [8]. Fig. 2a: 0 wt.% Cu.; Fig. 2b: 3 wt.% Cu.; Fig. 2c: 6 wt.% Cu.; Fig. 2d: 9 wt.% Cu.

As seen in figure 2 an increase in copper content does not necessarily mean linear increase in better melting properties. At 3 weight % best melting properties could be achieved. Additionally the before mentioned bloating behavior was at 3 weight % also the least. With increasing shares of Cu the melting ability declines again, most probably as result of an oversupply of reducing agents.

To figure out what influence the atmosphere takes places in melting trials, in figure 1b a comparison between heating microscope trials with inert and reducing (CO) atmospheres where analyzed. As seen, tests within the reducing atmosphere show a slightly lower starting point of melting activities and additionally also a lower maximum temperature for complete melting. This indicates strong influences of the prevailing atmospheres on the melting ability between inert and reducing atmospheres, thus changing the process window for the InduMelt plant to a lower needed temperature. Since there are no thermodynamic data such as kinetics available for LIB cathode material under reducing atmospheres, further tests using a simultaneous thermal analysis (STA) coupled with a Fourier transform infrared spectroscopy (FTIR) to analyze the resulting gas phase are intended.

CONCLUSION AND OUTLOOK

As can be seen within figure 1a/b and figure 2, the reducing atmosphere, as predominately occurring in the InduMelt plant, is decisive for further reduction and melting considerations. First of all, despite lower melting points, a specific temperature, of about 1342°C [9] is necessary for evaporation of Lithium and therefore generating the possibility to be extracted as gaseous particle. To validate necessary process parameters for reduction and melting abilities of LIB cathode material and active material, thermodynamic data such as reaction activities and kinetics have to be defined. Using a STA – FTIR these kind of data could be generated, resulting into better understanding of reaction mechanisms within the InduMelt, providing the possibility to optimize the design and functionality of the reactor.

Additionally, so far the influence of Cu on the melting ability has only been analyzed for the cathode material NCA. As tests from Baldauf [6] have shown, the cathode materials high temperature behavior strongly vary based on different concentrations of C and Al. Therefore, it can be assumed that also Cu will have different effects on the meltability of the cathode materials NMC, LCO and LFP.

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